VU VRIJE UNIVERSITEIT AMSTERDAM

VU Research Portal

Energy expressions in density-functional theory using line integrals.

van Leeuwen, R.; Baerends, E.J.

published in
Physical Review A. Atomic, Molecular and Optical Physics
1995

DOI (link to publisher)
10.1103/PhysRevA.51.170

document version
Publisher's PDF, also known as Version of record

Link to publication in VU Research Portal

citation for published version (APA)
van Leeuwen, R., & Baerends, E. J. (1995). Energy expressions in density-functional theory using line integrals. *Physical Review A. Atomic, Molecular and Optical Physics*, *51*, 170-178. https://doi.org/10.1103/PhysRevA.51.170

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

E-mail address:
vuresearchportal.ub@vu.nl

Download date: 05. May. 2023

PHYSICAL REVIEW A VOLUME 51, NUMBER 1 JANUARY 1995

Energy expressions in density-functional theory using line integrals

Robert van Leeuwen and Evert Jan Baerends
Afdeling Theoretische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands
(Received 17 March 1994)

In this paper we will address the question of how to obtain energies from functionals when only the functional derivative is given. It is shown that one can obtain explicit expressions for the exchange-correlation energy from approximate exchange-correlation potentials using line integrals along paths within the space of densities. The path dependence of the results is discussed and criteria for path independence are given. Derivations are given of upper and lower bounds to the exchange-correlation energy in terms of the exchange-correlation potential at the beginning and the end point of a certain path. We further express the kinetic part T_{xc} of the exchange-correlation energy in terms of a line integral and derive a constraint on approximate correlation potentials. We show how to use the line-integral formalism to derive the requirements that exchange-correlation potentials must fulfill in order to make the exchange-correlation functional satisfy some symmetry property such as rotational and translational invariance and scaling properties. Finally, we will discuss the use of line integrals along a path in density space to obtain energy differences, notably, the bonding energies of molecules, from exchange-correlation potentials. These last results generalize the transition-state formulations of Slater and Ziegler.

PACS number(s): 31.15.Ew

I. INTRODUCTION

In the last few years density-functional theory [1] has been successfully applied with increasing accuracy to systems ranging from atoms and molecules [2–4] to surfaces and solids [5]. Especially, the introduction of the so-called generalized gradient expansion approximations (GGA's) [6–10] for the exchange-correlation energy has constituted a great improvement over the local-density approximation (LDA) in the calculation of, for instance, molecular bond energies. In view of the accuracy of the GGA *energy* expressions for the exchange-correlation functional and their improvement over the LDA energy expressions, it is surprising that the GGA exchange-correlation *potential* gives little improvement over the LDA exchange-correlation potential [11,12] and has but a small influence on the density. For this reason calculating the GGA corrections from an LDA density yields almost the same results as an inclusion of the GGA potentials in a self-consistent calculation [13]. This fact is also reflected in the LDA+GGA eigenvalues being very close to the LDA eigenvalues, i.e., they are much too small for finite systems such as atoms and molecules and also for surfaces. As the eigenvalue of the highest occupied Kohn-Sham orbital has been proven to be equal to the ionization energy of the system [14,15], the LDA gives electrons that are too weakly bound. This latter fact is due to the LDA exchange-correlation potential having exponential decay instead of the correct Coulombic decay. One way to improve the one-electron energies and the density (and related quantities such as dipole moments) is to directly approximate the exchange or exchange-correlation potential instead of the exchange or exchange-correlation functional. Over the years several potentials (not only within density-functional theory) have been proposed. Well known is the average Hartree-Fock exchange potential proposed by Slater [16,17]. A so-called optimized effective potential (OEP) and an approximation to this was suggested by Sharp and Horton [18] and by Talman and Shadwick [19]. This potential received considerable attention within the context of exchange-only density-functional theory or the optimized effective potential model (OPM) and was shown to give one-electron energies close to the Hartree-Fock ones. An approximation to this potential was recently proposed by Krieger, Li, and Iafrate [20] and Gritsenko, van Leeuwen, and Baerends [21]. Also within the weighted density approximation (WDA) method approximate exchange potentials with the correct asymptotic behavior have been used [22–24]. A cruder way to improve the asymptotic behavior of the exchange potential was given by Latter [25] within the context of the Thomas-Fermi model, which, due to its simplicity, has found widespread use in atomic structure calculations. Much less work has been done regarding the full exchange-correlation potential. An approximate exchange-correlation potential has been proposed by Harbola and Sahni [26]. This exchange-correlation potential $v_{xc}(\mathbf{r})$ has been defined as the work done by bringing an electron from infinity to point $\mathbf{r}$ against the force of the electric field of the exchange-correlation hole. However, to insure path independence for nonspherical systems like molecules one must only consider the irrotational part of this electric field [27]. A gradient approximation to v_{xc} has recently been proposed in Ref. [12] that was shown to give very good ionization energies as calculated from the highest occupied Kohn-Sham orbital.

In view of the fact that correct one-electron energies, the asymptotic Coulombic behavior, and the atomic shell structure can be reasonably obtained by approximate po-

 ©1995 The American Physical Society

tentials, it is an interesting question of theoretical and practical importance whether we can calculate good exchange and correlation energies from these approximate potentials. This is also of importance since it is possible to test the quality of approximate exchange-correlation potentials by comparing them with accurate ones constructed from accurate densities. It is, for instance, an interesting question how certain features in the exchange-correlation potential (such as the bond midpoint peaks in molecules [28,29] related to the left-right correlation effect) contribute to the exchange-correlation energy. This requires an understanding of the relation between potential and energy expressions. A further understanding of the features displayed in the Kohn-Sham potential might then also lead to more improved expressions for the exchange-correlation energy. If we want to assign some energy expression, for instance, to the model potentials considered above, we immediately run into some theoretical difficulties because none of the potentials considered, with the exception of the OPM potential, is a functional derivative of some energy density functional. However, for approximate exchange potentials that satisfy the exchange scaling property it is still possible to assign an exchange energy using the Levy-Perdew relation [21,20]. However, such a relation is not available for the exchange-correlation potential due to the unknown scaling properties of the correlation functional. In Sec. II of this paper we will show how to use line integrals to calculate the exchange-correlation energy from an exchange-correlation potential. We also discuss some criteria of path independence. In Sec. III we discuss some bounds on the exchange-correlation energy in terms of the exchange-correlation potential and we give a line integral expression of the kinetic part $T_{\rm xc}$ of the exchange-correlation energy. In Sec. IV we derive some constraints on the correlation potential. In Sec. V we derive some properties with respect to rotation, translation, and scaling of the exchange-correlation energy from given properties with respect to these symmetries of the exchange-correlation potential. In Sec. VI we will address the question of how to calculate molecular bond energies from given potentials. Finally in Sec. VII we will present our conclusions.

II. LINE INTEGRALS AND PATH DEPENDENCE

In this section we will discuss the problem of obtaining energies from approximate potentials. The exchange-correlation energy for a system with Coulombic two-particle interactions is, within density-functional theory, usually defined as

$$E_{\rm xc}[\rho]=F[\rho]-T_s[\rho]-\tfrac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} , \quad (1)$$

where the universal functional F is as usual defined by a constrained search [30,31] over all antisymmetric wave functions yielding density ρ:

$$F[\rho]=\min_{\psi\to\rho}\langle\psi|\hat{T}+\hat{W}|\psi\rangle , \quad (2)$$

where $\hat{T}$ is the kinetic energy operator and $\hat{W}$ is the interparticle interaction operator. The Kohn-Sham kinetic energy $T_s[\rho]$ is the kinetic energy of a noninteracting particle system with the same density as the interacting system defined by

$$T_s[\rho]=\min_{\psi_s\to\rho}\langle\psi_s|\hat{T}|\psi_s\rangle=\langle\phi_s[\rho]|\hat{T}|\phi_s[\rho]\rangle , \quad (3)$$

where we search over all Slater determinants yielding density ρ and $\phi_s[\rho]$ is the Kohn-Sham determinant. The exchange energy functional is usually defined as [32]

$$E_x[\rho]=\langle\phi_s[\rho]|\hat{W}|\phi_s[\rho]\rangle-\tfrac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \quad (4)$$

and the correlation functional by

$$E_c[\rho]=E_{\rm xc}[\rho]-E_x[\rho] . \quad (5)$$

Suppose we have a parametrization $\gamma(t)$ of a set of electron densities starting at $\gamma(0)=\rho_1$ and ending in $\gamma(1)=\rho_2$. Suppose further that we have an exchange-correlation energy functional $E_{\rm xc}[\rho]$. Then we have

$$\begin{aligned} E_{\rm xc}[\rho_2]-E_{\rm xc}[\rho_1]&=\int_0^1 dt\frac{dE_{\rm xc}}{dt} \\ &=\int_0^1 dt\int d\mathbf{r}\frac{\delta E_{\rm xc}[\gamma(t)]}{\delta\rho(\mathbf{r})}\frac{d\gamma(t)}{dt} \\ &=\int_0^1 dt\int d\mathbf{r}\, v_{\rm xc}([\gamma(t)];\mathbf{r})\frac{d\gamma(t)}{dt} , \end{aligned} \quad (6)$$

in which $v_{\rm xc}$ is the functional derivative of $E_{\rm xc}$:

$$v_{\rm xc}([\rho];\mathbf{r})=\frac{\delta E_{\rm xc}}{\delta\rho(\mathbf{r})} . \quad (7)$$

If we take, for instance, the straight path from zero to ρ defined by $\gamma(t)=t\rho$ and we have $E_{\rm xc}(0)=0$ (which must be the case for any physically acceptable exchange-correlation functional), then $d\gamma/dt=\rho$ and it follows that

$$E_{\rm xc}[\rho]=\int d\mathbf{r}\,\rho(\mathbf{r})\varepsilon_{\rm xc}([\rho];\mathbf{r}) \quad (8)$$

in which $\varepsilon_{\rm xc}$ is defined as

$$\varepsilon_{\rm xc}([\rho];\mathbf{r})\equiv\int_0^1 dt\, v_{\rm xc}([t\rho];\mathbf{r}) . \quad (9)$$

This thus yields an explicit expression of the exchange-correlation energy in terms of the exchange-correlation potential. It should be remembered however that in this expression $v_{\rm xc}$ is a functional derivative. Suppose however that we only have an expression of $v_{\rm xc}$, for instance, in terms of the density and its gradients. Then we can define the line integral of $v_{\rm xc}$ along a path γ in the space of densities as

$$\int_\gamma v_{\rm xc}\equiv\int_0^1 dt\int d\mathbf{r}\, v_{\rm xc}([\gamma(t)];\mathbf{r})\frac{d\gamma(t)}{dt} . \quad (10)$$

As we can see from the above formulas the outcome of this line integral does not depend on the chosen path (except for the end points, of course) whenever $v_{\rm xc}$ is the functional derivative of some functional $E_{\rm xc}$. If one uses approximate potentials to obtain energy expressions this

way, one has to make sure that the result does not depend on the path γ. One therefore needs some criteria to determine whether v_{xc} yields path-independent line integrals. This is, for instance, the case when

$$\frac{\delta v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}')}-\frac{\delta v_{xc}(\mathbf{r}')}{\delta\rho(\mathbf{r})}=0\ , \tag{11}$$

which is a vanishing curl condition that is equivalent to

$$\frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}=\frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r}')\delta\rho(\mathbf{r})}\ . \tag{12}$$

To prove this we only have to show that a v_{xc} satisfying the above relation is the functional derivative of some functional E_{xc}. Suppose we *define* the functional E_{xc} by integrating v_{xc} along the straight path $\gamma(t)=t\rho$:

$$E_{xc}[\rho]\equiv\int d\mathbf{r}\,\rho(\mathbf{r})\varepsilon_{xc}([\rho];\mathbf{r})\ , \tag{13}$$

in which ε_{xc} is defined as in Eq. (9). If v_{xc} satisfies condition (11) then v_{xc} is the functional derivative of the above defined functional E_{xc} and hence path independent. This is readily shown by differentiation of the above Eq. (13). This yields

$$\begin{aligned}\frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}&=\varepsilon_{xc}([\rho];\mathbf{r})+\int d\mathbf{r}'\rho(\mathbf{r}')\frac{\delta\varepsilon_{xc}([\rho];\mathbf{r}')}{\delta\rho(\mathbf{r})}\\&=\varepsilon_{xc}([\rho];\mathbf{r})+\int_0^1 dt\int d\mathbf{r}'\rho(\mathbf{r}')\frac{\delta v_{xc}([t\rho];\mathbf{r}')}{\delta\rho(\mathbf{r})}\ .\end{aligned} \tag{14}$$

Now using condition (11) yields

$$\begin{aligned}\frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}&=\varepsilon_{xc}([\rho];\mathbf{r})+\int_0^1 dt\int d\mathbf{r}'t\rho(\mathbf{r}')\frac{\delta v_{xc}([t\rho];\mathbf{r})}{\delta[t\rho(\mathbf{r}')]}\\&=\varepsilon_{xc}([\rho];\mathbf{r})+\int_0^1 dtt\frac{dv_{xc}([t\rho];\mathbf{r})}{dt}\\&=\varepsilon_{xc}([\rho];\mathbf{r})+\int_0^1 dt\frac{d}{dt}\{tv_{xc}([t\rho];\mathbf{r})\}\\&\quad-\int_0^1 dtv_{xc}([t\rho];\mathbf{r})=v_{xc}([\rho];\mathbf{r})\ .\end{aligned} \tag{15}$$

Hence, v_{xc} obeying condition (11) is the functional derivative of the straight path E_{xc} defined in Eq. (13) and therefore yields path-independent line integrals.

We will now give another criterion for path independence related to Eq. (11). In order to do this we recall the Stokes theorem in vector calculus, which states for a vector field $\mathbf{v}$ in n-dimensional space

$$\sum_i^n\oint_\gamma v_i dx_i=\sum_{i,k}^n\int_S\left[\frac{\partial v_i}{\partial x_k}-\frac{\partial v_k}{\partial x_i}\right]dx_i dx_k\ , \tag{16}$$

in which γ is a closed curve which is the boundary of surface S. A generalization of this theorem to function spaces would be

$$\oint_\gamma\int d\mathbf{r}\,v\delta\rho(\mathbf{r})=\int_S\int\int d\mathbf{r}d\mathbf{r}'\left[\frac{\delta v(\mathbf{r})}{\delta\rho(\mathbf{r}')}-\frac{\delta v(\mathbf{r}')}{\delta\rho(\mathbf{r})}\right]\times\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')\ , \tag{17}$$

in which in the first integral the variations are restricted to be on the path γ and in the second integral on the surface S. From this equation we can see that if relation (11) is satisfied, then the integral of v along any closed path is zero and hence the line integral of v is path independent. On the other hand, if the line integral is zero for any closed path, then we obtain the integrability condition (11).

III. EXCHANGE-CORRELATION ENERGY AND THE KINETIC PART: BOUNDS FROM POTENTIALS

The present formalism can be used to obtain energy expressions from approximate potentials using line integrals. In order to obtain sensible results from such a calculation one has to make sure that any approximate v_{xc} is either a functional derivative [for instance, by requiring the integrability condition (11)] or that the approximate potential is a good approximation to the exact potential for every density along the integration path. This favors in practical applications some paths over other paths. For instance, the path defined by $\gamma(t)=t\rho$ has the disadvantage of not conserving the particle number, which can therefore be fractional, giving theoretical problems if one wants to assign a potential to the corresponding density. Another more appealing path choice is the following:

$$\gamma(t)=t^3\rho(t\mathbf{r})\ . \tag{18}$$

If we let the path parameter t run from 0 to 1, then we are integrating from 0 to ρ. The most important feature of this path is that it is particle number conserving; thus,

$$\int\gamma(t)d\mathbf{r}=\int\rho(\mathbf{r})d\mathbf{r}=N \tag{19}$$

along the path. For hydrogenlike atoms, for instance, we have

$$\gamma(t)=\frac{(tZ)^3}{\pi}e^{-tZr}\ , \tag{20}$$

in which Z is the nuclear charge. So if we let t approach zero, then the density $\gamma(t)$ becomes increasingly diffuse and approaches zero in every point of space while keeping its normalization. Our main task is now to construct for the case of many-electron systems exchange-correlation potentials which approximate the exact exchange-correlation potential along this path. Application of Eq. (6) for this path leads to the following expression for the exchange-correlation energy:

$$\begin{aligned}E_{xc}[\rho]&=\int_0^1 dt\int d\mathbf{r}\,v_{xc}([\gamma(t)];\mathbf{r})\\&\quad\times[3t^2\rho(t\mathbf{r})+t^3\mathbf{r}\cdot\nabla_{t\mathbf{r}}\rho(t\mathbf{r})]\\&=\int_0^1 dt\int d\mathbf{r}\frac{1}{t}v_{xc}\left[[\gamma(t)];\frac{1}{t}\mathbf{r}\right][3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]\end{aligned} \tag{21}$$

in which we performed the substitution $t\mathbf{r}\rightarrow\mathbf{r}$. Before we go on to discuss the exchange-correlation potential let us first discuss the simpler case of the exchange potential alone. Suppose we have an approximate exchange potential $\bar{v}_x$, for instance, of the form

$$\bar{v}_x(\mathbf{r})=\rho^{1/3}(\mathbf{r})f(x,y)\ , \tag{22}$$

where

$$x(\mathbf{r})=\frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \tag{23}$$

and

$$y(\mathbf{r})=\frac{\nabla^2\rho(\mathbf{r})}{\rho^{5/3}(\mathbf{r})} \tag{24}$$

are dimensionless functions. This approximate potential satisfies the following well-known scaling property [33] of the exchange potential:

$$v_x([\rho_t];\mathbf{r})=tv_x([\rho];t\mathbf{r}) , \tag{25}$$

in which $\rho_t=\gamma(t)$ is just the path of Eq. (18) [in the following we will, for notational convenience, use ρ_t instead of $\gamma(t)$ for this particular path]. Let v_x denote the exact exchange potential being the functional derivative of the exact exchange functional. The difference between the exact exchange energy $E_x[\rho]$ and the approximate exchange energy $\tilde{E}_x[\rho]$ using the line integral of Eq. (21) and scaling property (25) is then given by

$$E_x[\rho]-\tilde{E}_x[\rho]=\int_\gamma v_x-\int_\gamma \tilde{v}_x=\int d\mathbf{r}(v_x([\rho];\mathbf{r})-\tilde{v}_x([\rho];\mathbf{r}))[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] . \tag{26}$$

For a correctly scaling approximate exchange potential the difference in the two line integrals thus depends only on the difference between the two potentials at the end points of the path and can be made arbitrarily small by better fits of $\tilde{v}_x$ to v_x at this end point. This can be done, in practice, for instance, by fitting to the so-called optimized effective potential (OPM) [20,21]. To show that if $\tilde{v}_x$ is not a functional derivative we can make the difference in the line integral of v_x and $\tilde{v}_x$ arbitrarily large, we consider the following path:

$$\tilde{\gamma}(t)=t^3\rho(t\mathbf{r}+(1-t)\mathbf{R}) , \tag{27}$$

in which $\mathbf{R}$ is an arbitrary vector in three-dimensional space. We have

$$\begin{aligned}\frac{d\tilde{\gamma}(t)}{dt}=&3t^2\rho(t\mathbf{r}+(1-t)\mathbf{R})\\&+t^3\mathbf{r}\cdot\nabla_{t\mathbf{r}+(1-t)\mathbf{R}}\rho(t\mathbf{r}+(1-t)\mathbf{R})\\&-t^3\mathbf{R}\cdot\nabla_{t\mathbf{r}+(1-t)\mathbf{R}}\rho(t\mathbf{r}+(1-t)\mathbf{R}) .\end{aligned} \tag{28}$$

Integrating along this path (which can easily be checked to be particle number conserving) yields, using the fact that both the exact v_x and the approximate potential $\tilde{v}_x$ satisfy some translational invariance property [see Eq. (65) of Sec. V],

$$\begin{aligned}\int_{\tilde{\gamma}} v_x-\int_{\tilde{\gamma}}\tilde{v}_x=&\int d\mathbf{r}[v_x(\mathbf{r})-\tilde{v}_x(\mathbf{r})][3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]\\&-\mathbf{R}\cdot\int d\mathbf{r}[v_x(\mathbf{r})-\tilde{v}_x(\mathbf{r})]\nabla\rho(\mathbf{r}) .\end{aligned} \tag{29}$$

We see that this expression can be made arbitrarily large by choosing an arbitrarily large $\mathbf{R}$ (which amounts to choosing a different path) if the difference between v_x and $\tilde{v}_x$ is not zero.

Things are more complicated if we want to calculate the total exchange-correlation energy due to the fact that we do not know the scaling properties of the correlation potential. This means that we cannot calculate the exchange-correlation energy directly from the knowledge of $v_{xc}([\rho];\mathbf{r})$ alone; we must also know v_{xc} along some path $\gamma(t)$ in density space. However, some useful inequalities can be derived from the knowledge of $v_{xc}([\rho];\mathbf{r})$. Averill and Painter [34] and Levy and Perdew [32] have derived the following useful relation:

$$E_{xc}[\rho]=\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]-T_{xc}[\rho] , \tag{30}$$

where

$$T_{xc}[\rho]=T[\rho]-T_s[\rho] \tag{31}$$

is the kinetic part of the exchange-correlation energy. The kinetic energy $T[\rho]$ is as usual defined by

$$T[\rho]=\langle\psi[\rho]|\hat{T}|\psi[\rho]\rangle , \tag{32}$$

where $\hat{T}$ is the kinetic-energy operator and $\psi[\rho]$ is the antisymmetric wave function yielding density ρ and minimizing the universal functional $F[\rho]$. As can be inferred directly from Eq. (6) using the scalar path (18), it follows from Eq. (30) that equivalently

$$\begin{aligned}T_{xc}[\rho]=&\left.\frac{dE_{xc}[\gamma(t)]}{dt}\right|_{t=1}-E_{xc}[\rho]\\=&\left.\frac{dE_c[\gamma(t)]}{dt}\right|_{t=1}-E_c[\rho] ,\end{aligned} \tag{33}$$

which is a useful relation that can be used to obtain the kinetic-energy part of the exchange-correlation energy from approximate exchange-correlation or correlation functionals such as those used in LDA and GGA. Relation (30) is also useful to obtain an upper bound to the exchange-correlation energy from the knowledge of the exchange-correlation potential. From the definitions for $T[\rho]$ and $T_s[\rho]$ we can deduce the well-known result [1]

$$T_s[\rho]=\langle\phi_s[\rho]|\hat{T}|\phi_s[\rho]\rangle\le\langle\psi[\rho]|\hat{T}|\psi[\rho]\rangle=T[\rho] , \tag{34}$$

and thus $T_{xc}[\rho]\ge 0$ and we find the following inequality:

$$E_{xc}[\rho]\le\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] , \tag{35}$$

which provides an upper bound to E_{xc}. A similar inequality can be obtained for the correlation functional E_c (with corresponding correlation potential v_c being the functional derivative of E_c) by subtracting the Levy-Perdew relation (26) for the exchange from Eq. (30), which yields

$$E_c[\rho]=\int d\mathbf{r}\, v_c([\rho];\mathbf{r})[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]-T_{xc}[\rho]$$
$$\leq \int d\mathbf{r}\, v_c([\rho];\mathbf{r})[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] \ . \quad (36)$$

This gives an upper bound to the correlation energy when the correlation potential is known. To provide a lower bound to E_c in terms of potentials we use the following relation, which is valid for systems with Coulombic interparticle interactions proved by Levy [35]:

$$\lim_{t\to 0}\frac{1}{t}E_c[\rho_t]=-b[\rho] \ , \quad (37)$$

where $b[\rho]$ is a positive functional satisfying the following inequality:

$$T_{xc}[\rho]-E_c[\rho]\leq b[\rho]\leq\langle\phi_s[\rho]|\hat{W}|\phi_s[\rho]\rangle \ , \quad (38)$$

where $\phi_s[\rho]$ is the Kohn-Shamm determinant. Relation (37) immediately leads to

$$-b[\rho]=\lim_{t\to 0}\frac{1}{t}E_c[\rho_t]=\left.\frac{dE_c[\rho_t]}{dt}\right|_{t=0}$$
$$=\int d\mathbf{r}\,\hat{v}_c([\rho];\mathbf{r})\times[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] \ , \quad (39)$$

where

$$\hat{v}_c([\rho];\mathbf{r})=\lim_{\lambda\to 0}\frac{1}{\lambda}v_c\left[[\rho_\lambda];\frac{\mathbf{r}}{\lambda}\right] \ . \quad (40)$$

Combining relations (38) and (33) then gives

$$E_c[\rho]\geq\frac{1}{2}\left[\left.\frac{dE_c[\rho_t]}{dt}\right|_{t=0}+\left.\frac{dE_c[\rho_t]}{dt}\right|_{t=1}\right]$$
$$=\int d\mathbf{r}\tfrac{1}{2}\{\hat{v}_c([\rho];\mathbf{r})+v_c([\rho];\mathbf{r})\}\times[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] \ . \quad (41)$$

So we have now derived an upper and a lower bound to the correlation-energy functional in terms of the correlation potential. Adding the Levy-Perdew relation for the exchange potential on both sides of the inequalities gives corresponding bounds for the exchange-correlation energy:

$$\int d\mathbf{r}\tfrac{1}{2}\{\hat{v}_{xc}([\rho];\mathbf{r})+v_{xc}([\rho];\mathbf{r})\}[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]$$
$$\leq E_{xc}[\rho]\leq\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] \ , \quad (42)$$

where $\hat{v}_{xc}=v_x+\hat{v}_c$ (using $\hat{v}_x=v_x$ which is due to the exchange scaling property of v_x). So upper and lower bounds to the exchange-correlation energy can be given from the knowledge of the exchange-correlation potential at the beginning ($t=0$) and the end ($t=1$) of the scaling path. We will now give an expression for the kinetic part of the exchange-correlation energy. From relation (30) and Eq. (6)

$$T_{xc}[\rho]=\int d\mathbf{r}\{v_{xc}([\rho];\mathbf{r})-\bar{v}_{xc}([\rho]:\mathbf{r})\}[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] \ , \quad (43)$$

where

$$\bar{v}_{xc}([\rho];\mathbf{r})=\int_0^1 dt\frac{1}{t}v_{xc}\left[[\gamma(t)];\frac{\mathbf{r}}{t}\right] \ . \quad (44)$$

This gives an explicit expression for T_{xc} in terms of the exchange-correlation potential. It can therefore directly be calculated from approximate expressions of v_{xc} or from the knowledge of v_{xc} along the scaling path. As a result of the scaling property of the exchange potential the above equation can be further split up as follows:

$$\bar{v}_{xc}([\rho];\mathbf{r})=\int_0^1 dt\frac{1}{t}v_x\left[[\gamma(t)];\frac{\mathbf{r}}{t}\right]+\int_0^1 dt\frac{1}{t}v_c\left[[\gamma(t)];\frac{\mathbf{r}}{t}\right]$$
$$=v_x([\rho];\mathbf{r})+\int_0^1 dt\frac{1}{t}v_c\left[[\gamma(t)];\frac{\mathbf{r}}{t}\right]$$
$$=v_x([\rho];\mathbf{r})+\bar{v}_c([\rho];\mathbf{r}) \ , \quad (45)$$

where

$$\bar{v}_c([\rho];\mathbf{r})=\int_0^1 dt\frac{1}{t}v_c\left[[\gamma(t)];\frac{\mathbf{r}}{t}\right] \ . \quad (46)$$

This leads to another expression for T_{xc} in terms of the correlation potential

$$T_{xc}[\rho]=\int d\mathbf{r}[v_c([\rho];\mathbf{r})-\bar{v}_c([\rho];\mathbf{r})]\times[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] \ . \quad (47)$$

From $T_{xc}[\rho]\geq 0$ it follows further that

$$\int d\mathbf{r}\,\bar{v}_c([\rho];\mathbf{r})[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]$$
$$\leq\int d\mathbf{r}\, v_c([\rho];\mathbf{r})[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] \ , \quad (48)$$

which provides a further constrain on approximate correlation potentials. Further constraints are derived in the next section.

IV. CONSTRAINTS ON v_c

We now will derive some constraints on the correlation potential. Levy has proven the following useful relation [35], which is valid for systems with repulsive Coulombic interparticle interactions:

$$\lim_{t\to\infty}E_c[\rho_t]>-\infty \ . \quad (49)$$

Using relation (49) it then follows directly from

$$E_{xc}[\rho_t]=tE_x[\rho]+E_c[\rho_t] \quad (50)$$

that

$$E_x[\rho]=\lim_{t\to\infty}\frac{1}{t}E_{xc}[\rho_t] \ . \quad (51)$$

Equation (49) immediately leads to a constraint on the correlation potential. If we use the scaling path we find the following line integral:

$$E_c[\rho_\lambda]=\int_0^\lambda dt \int d\mathbf{r}\frac{1}{t}v_c\left[[\rho_t];\frac{\mathbf{r}}{t}\right][3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] . \tag{52}$$

Application of Eq. (49) then immediately gives

$$\int_0^\infty dt \int d\mathbf{r}\frac{1}{t}v_c\left[[\rho_t];\frac{\mathbf{r}}{t}\right][3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]>-\infty , \tag{53}$$

which puts constraints on approximate correlation potentials. The above constraint is, for example, not satisfied by the LDA correlation potential due to the logarithmic divergence of the LDA correlation energy as a function of the scaling parameter t. We can also write Eq. (51) in line integral form giving

$$E_x[\rho]=\lim_{\lambda\to\infty}\frac{1}{\lambda}\int_0^\lambda dt \int d\mathbf{r}\frac{1}{t}v_{xc}\left[[\rho_t];\frac{\mathbf{r}}{t}\right]\times[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] . \tag{54}$$

Inserting $v_{xc}=v_x+v_c$ in the above equation and using the scaling property of v_x we find the following constraint on v_c:

$$\lim_{\lambda\to\infty}\frac{1}{\lambda}\int_0^\lambda dt \int d\mathbf{r}\frac{1}{t}v_c\left[[\rho_t];\frac{\mathbf{r}}{t}\right][3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})]=0 . \tag{55}$$

The above constraint, which is weaker than constraint (53), follows also directly from constraint (53). The correlation potential of the local density approximation, for instance, satisfies the above Eq. (55) but not constraint (53).

V. INVARIANCE PROPERTIES OF POTENTIALS

The above formalism of line integrals provides an easy way to obtain conditions on the energy functional in the case that the exchange-correlation potential has some invariance or symmetry property. Suppose, for instance, that we vary the densities along our path γ by varying our path parameter t but that the potential v_{xc} has some symmetry property under such changes. Using Eq. (6) we then can deduce some properties of E_{xc}. In the following we will apply this idea to rotation, translation, and scaling properties of E_{xc}.

We define a path $\gamma(t)$ by

$$\gamma(t)=\rho(R(t)\mathbf{r}) , \tag{56}$$

where $R(t)$ is a rotation in three-dimensional space which rotates the vector $\mathbf{r}$ around a vector $\boldsymbol{\omega}$ by an angle t. If the functional E_{xc} is invariant under rotations we have that $E_{xc}[\gamma(t)]=E_{xc}[\rho]$ is constant as a function of t and we find

$$\begin{aligned}0&=\left.\frac{dE_{xc}[\gamma(t)]}{dt}\right|_{t=\theta}\\&=\int d\mathbf{r}\frac{\delta E_{xc}[\gamma(\theta)]}{\delta\rho(\mathbf{r})}\left.\frac{d\gamma(t)}{dt}\right|_{t=\theta}\\&=\int d\mathbf{r}\, v_{xc}([\gamma(\theta)];\mathbf{r})[\boldsymbol{\omega}\times R(\theta)\mathbf{r}]\cdot\nabla_{R(\theta)\mathbf{r}}\rho(R(\theta)\mathbf{r}) .\end{aligned} \tag{57}$$

For $\theta=0$ in particular we find

$$\begin{aligned}0&=\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})(\boldsymbol{\omega}\times\mathbf{r})\cdot\nabla\rho(\mathbf{r})\\&=\int d\mathbf{r}\, v_{xc}([\rho];R(\theta)\mathbf{r})\\&\quad\times(\boldsymbol{\omega}\times R(\theta)\mathbf{r})\cdot\nabla_{R(\theta)\mathbf{r}}\rho(R(\theta)\mathbf{r}) .\end{aligned} \tag{58}$$

The above Eqs. (57) and (58) yield the same result for all densities ρ and all rotations $R(\theta)$. We thus must have

$$v_{xc}([\rho(R(\theta)\mathbf{r})];\mathbf{r})=v_{xc}([\rho(\mathbf{r})];R(\theta)\mathbf{r}) . \tag{59}$$

So if we insert in v_{xc} the rotated density, then we obtain the same value in point $\mathbf{r}$ as v_{xc} with the original density in the rotated point $R(\theta)\mathbf{r}$ [33,12]. Alternatively, the line integral of Eq. (6) offers the possibilities of making statements about the energy functional when we know the properties of the potential. We can now prove the following statement. If a potential v_{xc} satisfies the rotation symmetry property of Eq. (59) and if v_{xc} is a functional derivative of some functional E_{xc}, then E_{xc} is rotationally invariant. To prove this we insert the path of Eq. (56) in Eq. (6), which gives

$$\begin{aligned}E_{xc}[\rho(R(\theta)\mathbf{r})]-E_{xc}[\rho(\mathbf{r})]&=\int_0^\theta dt \int d\mathbf{r}\, v_{xc}([\gamma(t)];\mathbf{r})(\boldsymbol{\omega}\times R(t)\mathbf{r})\cdot\nabla_{R(t)\mathbf{r}}\rho(R(t)\mathbf{r})\\&=\int_0^\theta dt \int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})(\boldsymbol{\omega}\times\mathbf{r})\cdot\nabla\rho(\mathbf{r})=\theta\boldsymbol{\omega}\cdot\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})\mathbf{r}\times\nabla\rho(\mathbf{r}) ,\end{aligned} \tag{60}$$

in which we in the second step used the rotation symmetry property of Eq. (59) and carried out a substitution $R(t)\mathbf{r}\to\mathbf{r}$. If we insert $\theta=2\pi$ in the above formula (60), then we are integrating along a closed path and we obtain

$$\oint_\gamma v_{xc}=2\pi\boldsymbol{\omega}\cdot\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})\mathbf{r}\times\nabla\rho(\mathbf{r}) . \tag{61}$$

As v_{xc} is a functional derivative the loop integral should be zero. This is also obvious from the left-hand side of Eq. (60) as the 2π-rotated density is equal to the starting density and we obtain

$$0=\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})\mathbf{r}\times\nabla\rho(\mathbf{r}) \tag{62}$$

for any density ρ. If we insert this equation back into Eq. (60), then we obtain

$$E_{xc}[\rho(R(\theta)\mathbf{r})]=E_{xc}[\rho(\mathbf{r})] , \tag{63}$$

which proves our statement.

We can carry out a similar derivation for the translation properties of the potential. If we define the path $\gamma(t)$ by

$$\gamma(t)=\rho(\mathbf{r}+t\mathbf{R}) , \tag{64}$$

in which $\mathbf{R}$ is an arbitrary translation vector and suppose that E_{xc} is translationally invariant, then we have that $E_{xc}[\gamma(t)]=E_{xc}[\rho]$ is constant as a function of t and we find by taking the derivative with respect to t at $t=1$ and $t=0$ that

$$v_{xc}([\rho(\mathbf{r}+\mathbf{R})];\mathbf{r})=v_{xc}([\rho(\mathbf{r})];\mathbf{r}+\mathbf{R}) . \tag{65}$$

Thus v_{xc} with the translated density inserted yield the same value in point $\mathbf{r}$ as v_{xc} with the original density inserted in point $\mathbf{r}+\mathbf{R}$ [12]. Using the line integral of Eq. (6) we now however also prove the opposite statement under some restrictions. If a potential satisfies relation (65) and if v_{xc} is a functional derivative of some functional E_{xc} which is bounded from above or below (the exact exchange-correlation functional is bounded from above as $E_{xc}\leq 0$), then this functional is translationally invariant. If we use the path of Eq. (64) and insert it in Eq. (6) we obtain

$$E_{xc}[\rho(\mathbf{r}+\mathbf{R})]-E_{xc}[\rho(\mathbf{r})] = \int_0^1 dt \int d\mathbf{r}\, v_{xc}([\gamma(t)];\mathbf{r})\mathbf{R}\cdot\nabla\rho(\mathbf{r}+t\mathbf{R}) . \tag{66}$$

If we use the translation symmetry property (65), we have

$$E_{xc}[\rho(\mathbf{r}+\mathbf{R})]-E_{xc}[\rho(\mathbf{r})]=\int_0^1 dt \int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r}+t\mathbf{R})\mathbf{R}\cdot\nabla\rho(\mathbf{r}+t\mathbf{R}) = \int_0^1 dt \int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})\mathbf{R}\cdot\nabla\rho(\mathbf{r})=\mathbf{R}\cdot\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})\nabla\rho(\mathbf{r}) , \tag{67}$$

in which we carried out a substitution $\mathbf{r}+t\mathbf{R}\rightarrow\mathbf{r}$, which makes the t integration trivial. The right-hand side of this equation can be made arbitrarily large (both positive and negative) by making $\mathbf{R}$ arbitrarily large. As E_{xc} is bounded from above or below this right-hand side of the equation must therefore by zero, which yields

$$\int d\mathbf{r}\, v_{xc}([\rho];\mathbf{r})\nabla\rho(\mathbf{r})=0 , \tag{68}$$

and therefore one has

$$E_{xc}[\rho(\mathbf{r}+\mathbf{R})]=E_{xc}[\rho(\mathbf{r})] . \tag{69}$$

We can carry out a similar analysis for scaling properties. We then define a path

$$\gamma(t)=t^3\rho(t\mathbf{r}) . \tag{70}$$

Suppose we have an energy functional E with functional derivative v which satisfies the following scaling relation:

$$E[\gamma(t)]=t^nE[\rho] , \tag{71}$$

with n some positive integer. By differentiating the above equation in $t=1$ and $t=\lambda$ one derives

$$v([\lambda^3\rho(\lambda\mathbf{r})];\mathbf{r})=\lambda^n v([\rho];\lambda\mathbf{r}) . \tag{72}$$

This result has been derived before [33], but is presented here to motivate our following statement. If a potential v satisfies the scaling relation (72) and is the functional derivative of some functional E with $E[0]=0$, then this functional satisfies the scaling property (71). If we use the line integral of Eq. (6) and insert the path of Eq. (70) we obtain

$$E[\gamma(\lambda)]-E[0]=\int_0^\lambda dt \int d\mathbf{r}\, v([\gamma(t)];\mathbf{r})[3t^2\rho(t\mathbf{r})+t^3\mathbf{r}\cdot\nabla_{t\mathbf{r}}\rho(t\mathbf{r})] . \tag{73}$$

If we now use the scaling property (72), we have, after a substitution,

$$E[\gamma(\lambda)]-E[0]=\int_0^\lambda dt \int d\mathbf{r}\, t^{n-1}v([\rho];\mathbf{r}) \times[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] =\frac{\lambda^n}{n}\int d\mathbf{r}\, v([\rho];\mathbf{r})[3\rho(\mathbf{r})+\mathbf{r}\cdot\nabla\rho(\mathbf{r})] . \tag{74}$$

Hence we have

$$E[\gamma(\lambda)]-E[0]=\lambda^n\{E[\gamma(1)]-E[0]\} . \tag{75}$$

In this equation $E[0]$ is just an integration constant. For instance, if we add to the functional (71) an arbitrary constant, then it will satisfy the above Eq. (75) and its potential will still satisfy (72). So, if we set $E[0]=0$, then we obtain

$$E[\lambda^3\rho(\lambda\mathbf{r})]=\lambda^nE[\rho(\mathbf{r})] , \tag{76}$$

which proves our statement.

VI. CALCULATING MOLECULAR BINDING ENERGIES FROM POTENTIALS

One of the most successful applications of density-functional theory has been the calculation of molecular binding energies. This is largely due to the development of gradient corrected functionals. However, the potentials corresponding to these functionals are not much improved [12], proving that the functionals still deviate considerably from the exact one. Since the exact functional is unknown, whereas the exact (or at least an accurate) potential can be obtained from an accurate density [12], an improvement of the existing gradient corrections might be sought in the development of better potentials in combination with a calculation of the energy from the potential. In this section we will discuss how to obtain energy differences from potentials. Suppose we have a diatomic molecule consisting of atom A and atom B. The total density of the molecule is given by $\rho_M=\rho_\Sigma+\Delta\rho$, where $\rho_\Sigma=\rho_A+\rho_B$ is the sum of atomic densities and $\Delta\rho$ is the deformation density of the molecule. The binding

energy contribution of the exchange-correlation energy is then given by

$$\Delta E_{\rm xc}=E_{\rm xc}[\rho_M]-E_{\rm xc}[\rho_A]-E_{\rm xc}[\rho_B]$$
$$=(E_{\rm xc}[\rho_M]-E_{\rm xc}[\rho_\Sigma])$$
$$+(E_{\rm xc}[\rho_\Sigma]-E_{\rm xc}[\rho_A]-E_{\rm xc}[\rho_B])\ . \quad (77)$$

The first term between brackets we will call ΔE_1 and the second term between brackets we will call ΔE_2. The term ΔE_1 refers to an energy difference where the nuclear framework and therefore the cusps in the density do not change, only the density $\rho(\mathbf{r})$ changes. An analogous situation holds for energy differences relating to ionization and excitation energies. This division of the total bond energy has been applied for the first time in connection with the transition-state method for bond energies developed by Ziegler and Rauk [36], in which ΔE_1 is calculated using a Taylor expansion of $E_{\rm xc}[\rho]$ around the "transition" density $\rho_T=\frac{1}{2}(\rho_\Sigma+\rho_M)$. Ziegler used a Taylor expansion in density-matrix elements $P_{\mu\nu}$, which generalized the transition-state method of Slater [39] who used a Taylor expansion in orbital occupations. The calculation of ΔE_2 has until now been carried out using explicit expressions for $E_{\rm xc}[\rho]$ as integrals over approximate (LDA or GGA) energy densities, the integrations being performed by three-dimensional numerical integration. We note in passing that an analogous division in two terms, using the intermediate density, ρ_Σ is also useful for other energy terms such as the electrostatic ones, enabling one to achieve numerical precision by an adequate division between analytically and numerically calculated parts [37].

We address in this section the problem of calculating the two energy terms when only the potential is known. The first term ΔE_1 can in practice be calculated accurately using the linear path [37,38]

$$\gamma(t)=\rho_\Sigma+t(\rho_M-\rho_\Sigma)=\rho_\Sigma+t\Delta\rho\ , \quad (78)$$

which yields

$$\Delta E_1=\int_0^1 dt\int d\mathbf{r}\, v_{\rm xc}([\gamma(t)];\mathbf{r})\Delta\rho(\mathbf{r})$$
$$=\int d\mathbf{r}\Delta\rho(\mathbf{r})\int_0^1 v_{\rm xc}([\gamma(t)];\mathbf{r})dt\ . \quad (79)$$

When using a simple Simpson rule for the t-integration one obtains

$$\Delta E_1=\int d\mathbf{r}\,\Delta\rho(\mathbf{r})(\tfrac{1}{6}v_{\rm xc}([\rho_\Sigma];\mathbf{r})+\tfrac{2}{3}v_{\rm xc}([\rho_T];\mathbf{r})$$
$$+\tfrac{1}{6}v_{\rm xc}([\rho_M];\mathbf{r}))\ , \quad (80)$$

where $\rho_T=\gamma(\frac{1}{2})=\frac{1}{2}(\rho_\Sigma+\rho_M)$ is the so-called transition-state density. This procedure actually proves to be exactly equivalent to the transition-state method [36] carried through to third order in $\delta\rho$. It may easily be extended to higher accuracy by using the higher-order numerical quadrature in t, but this is usually not necessary. For practical applications of the above method with approximate exchange-correlation potentials it is necessary that the approximate potential give a good description of the real exchange-correlation potential along the path in ρ space that is defined by Eq. (78).

The other part of the binding energy ΔE_2 also has to be calculated from the potential if explicit exchange-correlation energy expressions are not known. One way to do this is just to calculate the total energies of the atom and the molecule using Eqs. (8) and (9) and to calculate the difference. This procedure has, however, some disadvantages. First of all, along the path $\gamma(t)=t\rho$ the number of particles is not conserved, which presents some difficulties from a theoretical point of view. Second, if one makes an approximate expression for the potential v for some N-electron system, for instance, by a fitting procedure to some known exact potential, one makes unknown errors for systems with a different number of electrons. It is therefore of some advantage to use particle number conserving paths. Therefore, to calculate the energy difference ΔE_2 one might consider the following path:

$$\gamma_\Sigma(t)=\rho_A(\mathbf{r})+\rho_B(\mathbf{r}+t\mathbf{R})\ , \quad (81)$$

in which we let t run from 1 to ∞ and $\mathbf{R}$ is the internuclear distance. This path is particle number conserving. If we have $\rho_\Sigma=\gamma(1)$, then

$$\Delta E_2=\int_{\gamma_\Sigma} v_{\rm xc}$$
$$=\int d\mathbf{r}\int_\infty^1 dt v_{\rm xc}([\gamma_\Sigma(t)];\mathbf{r})\mathbf{R}\cdot\nabla\rho_B(\mathbf{r}+t\mathbf{R})\ . \quad (82)$$

Application of the above formula puts some severe restrictions on approximate exchange-correlation potentials. This approximate potential should give a good description of the exact $v_{\rm xc}$ at all bond distances. For instance, the bond midpoint peak in $v_{\rm xc}$ in dissociating molecules [28,29] must also be described by this approximate $v_{\rm xc}$. This might be feasible, for instance, in a gradient expansion using Laplacians of the density in any approximate $v_{\rm xc}$. However, care should be taken for potentials which are not functional derivatives, as in that case the value of ΔE_2 will depend on the dissociation path taken.

VII. CONCLUSIONS

In this work we addressed the question of how to obtain exchange-correlation energies from (approximate) exchange-correlation potentials. This is of some theoretical and practical importance as many approximate exchange and correlation potentials have been proposed. It is shown that one can use line integrals to express the exchange-correlation energy in terms of the exchange-correlation potentials. It was further shown how to derive symmetry properties of the exchange-correlation energy functional from the corresponding properties of the exchange-correlation potential. We further obtained some upper and lower bounds to the exchange-correlation energy which can be calculated if the exchange-correlation potential is known in two limiting cases, at the beginning and the end of the scaling path. We showed how to express the kinetic part $T_{\rm xc}$ of the exchange-correlation energy in terms of line integrals over the exchange-correlation $v_{\rm xc}$ or correlation potential

v_c and derived some constraints on the correlation potential. We finally addressed the problem of calculating the exchange-correlation part of molecular binding energies from approximate potentials. The constraints and inequalities derived in this article might prove useful to the development of more accurate exchange-correlation potentials improving the LDA and GGA potentials. Work along this line is in progress.

[1] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1990).
[2] L. Fan and T. Ziegler, J. Chem. Phys. **95**, 7401 (1991).
[3] A. D. Becke, J. Chem. Phys. **96**, 2155 (1992).
[4] B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. **98**, 5612 (1992).
[5] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[6] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[7] D. C. Langreth and J. Mehl, Phys. Rev. B **28**, 1809 (1983).
[8] J. P. Perdew and Wang Yue, Phys. Rev. B **33**, 8800 (1986).
[9] J. P. Perdew, Physica B **172**, 1 (1991).
[10] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[11] E. Engel, J. A. Chevary, L. D. Macdonald, and S. H. Vosko, Z. Phys. D **49**, 2421 (1994).
[12] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
[13] L. Fan and T. Ziegler, J. Chem. Phys. **94**, 6057 (1991).
[14] C. O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).
[15] M. Levy, J. P. Pewdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).
[16] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[17] O. L. Malkina, O. V. Gritsenko, and G. M. Zhidomirov, Chem. Phys. Lett. **171**, 191 (1990).
[18] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).
[19] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[20] J. B. Krieger, Yan Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).
[21] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends (unpublished).
[22] H. Przybylski and G. Borstel, Solid State Commun. **49**, 317 (1984).
[23] H. Przybylski and G. Borstel, Solid State Commun. **52**, 713 (1984).
[24] M. D. Glossman, L. C. Balbás, A. Rubio, and J. A. Alonso, Int. J. Quantum Chem. **49**, 171 (1994).
[25] R. Latter, Phys. Rev. **99**, 510 (1955).
[26] M. K. Harbola and V. Sahni, Phys. Rev. Lett. **62**, 489 (1989).
[27] M. K. Harbola, M. Slamet, and V. Sahni, Phys. Lett. A **157**, 60 (1991).
[28] M. A. Buijse, E. J. Baerends, and J. G. Snijders, Phys. Rev. A **40**, 4190 (1989).
[29] R. van Leeuwen and E. J. Baerends, Int. J. Quantum. Chem. **52**, 696 (1994).
[30] M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979).
[31] E. Lieb, Int. J. Quantum. Chem. **24**, 243 (1982).
[32] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).
[33] Hui Ou-Yang and M. Levy, Phys. Rev. Lett. **65**, 1036 (1990).
[34] F. W. Averill and G. S. Painter, Phys. Rev. B **24**, 6795 (1981).
[35] M. Levy, Phys. Rev. A **43**, 4637 (1991).
[36] T. Ziegler and A. Rauk, Theor. Chim. Acta **46**, 1 (1977).
[37] E. J. Baerends (unpublished).
[38] P. M. Boerrigter, Ph.D. thesis, Vrije Universiteit, Amsterdam, The Netherlands, 1987.
[39] J. C. Slater, *The Self-Consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974).